

Synthesis and Properties of Sulfated Alkanolamides¹ 3267

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Abstract

High purity alkanolamides were prepared by the sodium catalyzed reaction of methyl stearate, methyl palmitate and methyl laurate with ethanolamine, 2-hydroxypropylamine, 3-hydroxypropylamine and N-methyl N-hydroxyethylamine. The effect of structure on the surface active properties of the sulfation products was investigated. Stability studies showed that sulfated N-methyl N-hydroxyethylstearamide hydrolyzed rapidly by first order kinetics in acid or base. Sulfated hydroxyalkyl primary amides hydrolyzed slower in basic media following second order kinetics. Methyl groups attached to the N atom or to C in the short aliphatic chain improved solubility but had little effect on critical micelle concentration. The alkanolamides of palmitic and stearic acids were good detergents and lime soap dispersing agents.

Introduction

The ether alcohol sulfates of tallow alcohols have good solubility and detergent properties and are excellent lime soap dispersants when the degree of oxyalkylation is near one oxyalkyl group (6,7). Related compounds may be made by the reaction of amides with a mole of epoxide prior to sulfation, or more conveniently by the reaction of alkanolamines with fatty acids or esters (3).

Although the hydroxyethylamides and hydroxypropylamides have been prepared (1), literature describing the preparation and properties of their sulfates is limited to a few examples (2,5). Paquot (4) has studied the stability of mixed sulfated hydroxyethylamides in solutions of different pH. Desnuelle and Micaelli (2) have proposed that the sulfated N-(2-hydroxyethyl)-lauramide is made less stable by a neighboring group effect and shown that sulfated N-(3-hydroxypropyl)-lauramide is considerably more stable. The purpose of this paper is to study the effect of chemical structure of sulfated alkanolamides on surface active properties and stability to hydrolysis.

Experimental Procedures

Materials

Purified lauric, palmitic and stearic acids were converted to methyl esters and distilled. Vapor phase chromatography showed all esters to be better than 99% pure.

Alkanolamines were the best available commercial material, redistilled at 10 mm through a 1 ft column packed with a stainless steel protruded packing. Since the success of the reaction depended on the reactants being completely dry, an azeotropic distillation with toluene was sometimes helpful.

Amidations

The preparation of N-(2-hydroxyethyl)palmitamide is a typical amidation and is described as an example. Methyl palmitate, 86.0 g (0.318 mole), and 21.3 g (0.349 mole) ethanolamine were heated to 100 C.

Freshly cut sodium, 0.25 g, was added and the reaction mixture stirred and heated at 115–125 C for 40 min. The reaction flask was fitted with a condenser and side arm for collection of distillate. Heating was continued until methanol ceased to be collected. The reaction product was dissolved in 1500 ml of hot absolute ethanol, clarified by hot filtration, and chilled to room temperature. Crystallized solid, mp 98.7–99.5 C, was collected in 91% yield.

Substituted alkanolamides were generally more soluble than the example cited and it was often necessary to carry out crystallization at a lower temperature. Average deviation of the analytical values from theoretical was 0.12% with a maximum deviation of 0.46% for carbon, 0.26% for hydrogen and 0.13% for nitrogen.

Sulfations

To illustrate the sulfation procedure, the preparation of neutral sulfated N-(2-hydroxypropyl)palmitamide is described. The alkanolamide, 14.7 g (0.047 mole) was dissolved in 100 ml of chloroform and 7.8 g (0.067 mole) of chlorosulfonic acid was added dropwise with stirring while maintaining the temperature below room temperature with an ice bath. Stirring at 25 C was continued for 10 min after HCl evolution stopped. The reaction mixture was chilled, diluted with an equal volume of cold 95% ethanol and neutralized with 18 N NaOH. A crude product was obtained in 90% yield from this solution after clarification. Recrystallization from 150 ml of ethanol and 100 ml of chloroform gave 70% yield of a purified product (Systematic name N-2-hydroxypropylhexadecanamide H sulfate, Na salt.)

Average deviations of the analysis from theory for the sulfated products was 0.11% for carbon, 0.14% for hydrogen, 0.07% for nitrogen, and 0.12% for sulfur.

Hydrolysis Studies

Acid hydrolysis was measured in a hot mixture of 50 ml of 0.1 N HCl and 50 ml of 0.1 N neutral sulfated alkanolamide. Temperature was maintained at 80 C and 10 ml samples were withdrawn and titrated at suitable intervals. Amount of reaction, x , was determined from the increase in acidity and first order kinetics were calculated according to the equation, $k_1 = 1/t \ln a/(a-x)$. Time for 50% hydrolysis was determined from the $\log(a-x)$ vs. t plot, assuming hydrolysis at only one location in the molecule.

Alkaline hydrolysis was measured in a hot mixture of 50 ml of 0.1 N NaOH and 50 ml of 0.1 N neutral sulfated alkanolamide. Temperature was maintained at 100 C, and samples were withdrawn and titrated at suitable intervals. Concentration of unreacted product, $a-x$, was determined from the amount of alkali titratable and, where applicable, second order kinetics were calculated according to the equation, $k_2 = 1/t \cdot (x)/(a)(a-x)$. Time for 50% hydrolysis was determined from the $1/(a-x)$ vs. t plot assuming only one hydrolysis of the molecule. Since the measurement was made at the best straight portion of the curve rather than starting at 0.05 mole/liter, these values will be somewhat greater than the calculated.

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TABLE I
Hydrolysis of Sulfated Alkanolamides

	0.05 N Amide in 0.05 N NaOH 100 C			0.05 N Amide in 0.05 N HCl 80 C		
	k ₂ liters/ mole/ min	t _{1/2} min	Products, Fatty acid, %	k ₁ min-1	t _{1/2} min	Products, Fatty acid, %
C ₁₅ H ₃₁ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	0.032	>500	35	0.0029	180	50
C ₁₇ H ₃₅ CONHCH ₂ CH ₂ (CH ₃)OSO ₃ Na	0.17	126	25	0.0090	85	85
C ₁₁ H ₂₃ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	0.22	83	16	0.0042	142	40
C ₁₅ H ₃₁ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	0.22	83	0.0083	83	65
C ₁₇ H ₃₅ CON(CH ₃)CH ₂ CH ₂ OSO ₃ Na	(k ₁ = 0.082)	9	4	0.014	45	22

Surface Active Properties

Methods for the evaluation of surface active properties have been described in a previous publication (6). Krafft point is the temperature at which a 1% solution becomes clear on gradual heating, critical micelle concentration was determined by dye titration, Wilkes and Wickert's method was used for calcium stability, Borghetty and Bergman's method for lime soap dispersing power, Ross-Miles' test for foaming, and detergency was run in the Terg-O-Tometer.

Results and Discussion

A survey of methods for making high purity alkanolamides showed that the alkaline catalyzed reaction of alkanolamines with fatty esters gave the best yield of high purity product. Purity of the alkanolamides was checked by IR and elemental analysis. The products were found to be free of ester adsorption at 5.7 microns and analyses for C, H, N were in good agreement with theoretical values. Melting points of the ethanolamides and isopropanolamides, recorded on Table II, were found to be higher than those reported by D'Alelio and Reid (1). Reaction of fatty acid with alkanolamine either with or without a catalyst gave lower yields of product which showed ester adsorption in the IR spectra.

All reactants should be kept completely dry to avoid formation of alkali which would react with ester. Thus freshly cut sodium was used instead of sodium methoxide because it could be more surely added as a dry catalyst. Glycerol esters can be used as well as methyl esters in this reaction.

Hydrolysis Studies

Table I shows the hydrolysis constants, half life, and analysis of hydrolysis products for each of the sulfated alkanolamide structures. Reaction rate constants are not strictly valid because they are based on the assumption that hydrolysis is taking place at

only one location and it is known from analysis of products that hydrolysis takes place at both amide and sulfate locations. The values that are calculated however do serve as a comparative measure of ease of hydrolysis. Since the two reactions are additive and of the same order, the total rate equation can usually be plotted. An estimate of the relative contribution of each hydrolysis can be made from the analysis of products.

Alcohol sulfates are usually hydrolyzed by acid but are stable to basic hydrolysis. Table I shows that the sulfated alkanolamides can be hydrolyzed in alkaline as well as acid media and some of the hydrolysis takes place at the sulfate ester. It is believed therefore that a neighboring group effect may be important in this hydrolysis. Desnuelle and Micaelli (2) have proposed an oxazoline intermediate in this hydrolysis, explaining the greater stability of the sulfated N-(3-hydroxypropyl)lauramide by its greater difficulty in forming the heterocyclic ring.

Sulfated N-methyl-N-(2-hydroxyethyl)stearamide did not hydrolyze in alkali according to second order kinetics as expected. This compound hydrolyzed by first order kinetics in alkaline, acid, or neutral media and all reactions proceeded at a relatively rapid rate.

The acid hydrolysis rate for sulfated N-(3-hydroxypropyl)palmitamide was nearly the same as that for sodium hexadecyl sulfate (0.0037 min⁻¹) and less than that for sulfated oxyethylated octadecanol (0.0051 min⁻¹). The secondary sulfate from N-(2-hydroxypropyl)stearamide was found to hydrolyze at about the same rate as the primary sulfate from N-(2-hydroxyethyl)palmitamide. The high content of fatty acid in the acid hydrolyzed product suggests that the nearby sulfate groups aid in the amide hydrolysis.

Surface Active Properties

Table II lists the surface active properties of the sulfated alkanolamides and the melting points of the

TABLE II
Surface Active Properties

	Melting point of parent alkanolamide C	Krafft point, 1% C	Critical micelle concentration millimoles/ liter	Calcium stability ppm	Lime soap dispersing power, %	0.05% + .20% Builder 60 C, 300 ppm	
						Foam height mm	Detergency ΔR
C ₁₁ H ₂₃ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	89	14	10.1	1300	8	110	16
C ₁₅ H ₃₁ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	99	42	0.55	615 ^a	4	225	30
C ₁₇ H ₃₅ CONHCH ₂ CH ₂ CH ₂ OSO ₃ Na	103	53	0.16 ^a	570 ^a	5	195	32
C ₁₁ H ₂₃ CONHCH ₂ CH ₂ CH ₂ CH ₂ OSO ₃ Na	77	21	8.4	>1800	5	155	16
C ₁₅ H ₃₁ CONHCH ₂ CH ₂ CH ₂ CH ₂ OSO ₃ Na	92	47	0.45 ^a	515 ^a	4	225	30
C ₁₇ H ₃₅ CONHCH ₂ CH ₂ CH ₂ CH ₂ OSO ₃ Na	97	57	0.13 ^a	1800 ^a	5	185	31
C ₁₁ H ₂₃ CONHCH ₂ CH ₂ (CH ₃)OSO ₃ Na	70	<0	9.3	1800	7	153	15
C ₁₅ H ₃₁ CONHCH ₂ CH ₂ (CH ₃)OSO ₃ Na	80	<0	0.47	1800	4	220	29
C ₁₇ H ₃₅ CONHCH ₂ CH ₂ (CH ₃)OSO ₃ Na	86	27	0.14	1800 ^a	5	185	30
C ₁₁ H ₂₃ CON(CH ₃)CH ₂ CH ₂ CH ₂ OSO ₃ Na	20	<0	5.8	1800	8	200	22
C ₁₅ H ₃₁ CON(CH ₃)CH ₂ CH ₂ CH ₂ OSO ₃ Na	47	<0	0.41	1800	5	200	23
C ₁₇ H ₃₅ CON(CH ₃)CH ₂ CH ₂ CH ₂ OSO ₃ Na	55	21	0.11	1800	6	175	22
C ₁₅ H ₃₁ CON(CH ₃)CH ₂ CH ₂ CH ₂ OSO ₃ Na	32	0.75	>1800	7	220	27
C ₁₂ H ₂₅ OSO ₃ Na	24	16	6.3	650	30	185	15
C ₁₅ H ₃₁ OSO ₃ Na	58	56	0.11 ^a			190	33
C ₁₅ H ₃₁ OCH ₂ CH(CH ₃)OSO ₃ Na	39	43	0.11			100	31

^a Run at elevated temperature.

corresponding parent alkanolamides. Unlike the ether alcohol series (7) there is no relation between the melting point of the alkanolamide and the Krafft point of the sulfated alkanolamide. Sulfated N-(3-hydroxypropyl)stearamide has the highest Krafft point but there are several alkanolamides which melt higher than the corresponding parent alkanolamide including N-(2-hydroxyethyl)palmitamide which melts 15 degrees higher. Sulfated N-(2-hydroxyethyl)lauramide has a Krafft point of only 14 C although the melting point of the alkanolamide is 89 C.

Comparison of critical micelle concentration values shows that substitution at the alkyl portion of the amide has little effect. The presence of a methyl group, attached to C or N, had little effect on the critical micelle concentration. The cmc was about the same for all derivatives of a particular fatty acid. This seems to indicate that the amide group orients at the interface along with the main hydrophilic sulfate groups. Critical micelle concentrations of nearly all of the sulfated alkanolamides are slightly higher than alcohol sulfates having the same hydrocarbon chain length.

Measurement of surface tension of 0.1% solutions of the palmitic and stearic acid derivatives by the duNoüy method gave values of 41 to 43 dynes per

centimeter and interfacial tension against petrolatum for the same solutions were 10 to 12 dynes per centimeter. All of the sulfated alkanolamides were found to have good stability to calcium ion and to be effective lime soap dispersing agents. None of them showed unusual wetting properties. All sulfated alkanolamides from palmitic and stearic acids had good foam height and were effective detergents except those compounds which were not very stable to hydrolysis under washing conditions.

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